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New Method for the Estimation of Viscosity of Pure and Mixtures of Ionic Liquids Based on the UNIFAC−VISCO Model

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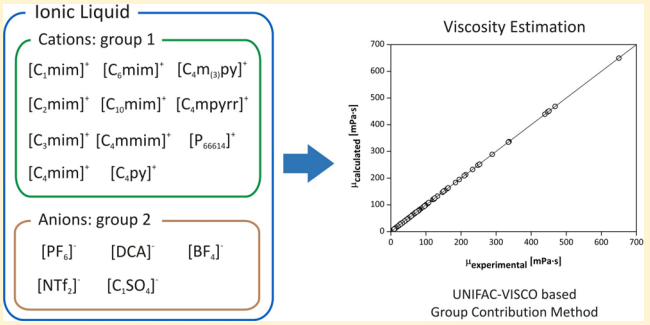
Supporting Information

ABSTRACT: A modified UNIFAC−VISCO group contribution method was developed for the correlation and prediction of viscosity of ionic liquids as a function of temperature at 0.1 MPa. In this original approach, cations and anions were regarded as peculiar molecular groups. The significance of this approach comes from the ability to calculate the viscosity of mixtures of ionic liquids as well as pure ionic liquids. Binary interaction parameters for selected cations and anions were determined by fitting the experimental viscosity data available in literature for selected ionic liquids. The temperature dependence on the viscosity of the cations and anions were fitted to a Vogel−Fulcher−Tamman behavior. Binary interaction parameters and VFT type fitting parameters were then used to determine the viscosity of pure and mixtures of ionic liquids with different combinations of cations and anions to ensure the validity of the prediction method. Consequently, the viscosities of binary ionic liquid mixtures were then calculated by using this prediction method. In this work, the viscosity data of pure ionic liquids and of binary mixtures of ionic liquids are successfully calculated from 293.15 K to 363.15 K at 0.1 MPa. All calculated viscosity data showed excellent agreement with experimental data with a relative absolute average deviation lower than 1.7%.



1. INTRODUCTION

Ionic liquids (ILs) with negligible vapor pressure at ambient temperature and pressure have made them potential greener alternatives to current solvents. Recent advances have been focused on developing new ILs for use in chemical synthesis, catalysis, and fuel cells.[1] ILs are composed of cations and anions; where the cations are typically bulky, asymmetrical, and organic.[2,3] Nevertheless, the corresponding anions can be either organic or inorganic.[4] The specific chemical and physical properties exhibited by an IL are determined by its particular cation−anion combination. It is theoretically possible to tailor an IL to possess a certain desired set of physical properties by altering its constituent cation−anion pair,[5] which are often referred to task-specific ILs.[6,7]

Because of the exceedingly large number of potential cation−anion combinations that can be used to synthesize ILs, searching via trial and error for an IL that exhibits the particular set of properties required for a given application at a given temperature and pressure would be impractical, time-consuming, and expensive.[4,8] A generic, reliable, and practical method of finding an IL with specific chemical and physical properties is essential to realize the commercial potential of ILs. A practical approach would be to use correlative and/or predictive models.

Viscosity is one of the most widely investigated physical properties, which is of utmost importance for any application. To date, various correlative models used to describe the effect of the temperature on ILs viscosity are reported in the literature, which are mainly based on different equations, such as Vogel−Fulcher−Tamman (VFT) equation,[9−11] Litovitz equation,[11,12] Arrhenius equation,[11] fluidity equation,[11] and power law equation.[13] Other approaches reported in the literature to describe the ILs viscosity are based on quantitative structure−property relationship (QSPR) methods.[14−17] For example, Bini et al.[14] reported a QSPR method for the correlation of the viscosity of bis(trifluoromethylsulfonyl)-imide-based ionic liquids with 32 different cations at 293 and 353 K separately. The accuracy of this correlation method was temperature dependent. A four-descriptor model was used for the correlation of viscosity at 293 K with R^2 (coefficient of determination) being 0.8755, and the fit was not satisfactory. An R^2 of 0.8982 was obtained for the three-descriptor model at 353 K, and the fit was visually more convincing. Furthermore, Han et al.[15] proposed a QSPR method for the prediction of the viscosity of imidazolium-based ionic liquids. Four data sets ($[BF_4]^-$, $[NTf_2]^-$, $[C_4mim]^+$, and $[C_2mim]^+$ based ILs) at ambient conditions were correlated with $R^2 > 0.93$. Similarly, Chen et al.[16] developed a simplified QSPR for the viscosity of

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Table 1. Selected Ions, ILs, and References from Which Experimental Data Were Collected

anion \ Cation	$[C_1mim]^+$	$[C_2mim]^+$	$[C_3mim]^+$	$[C_4mim]^+$	$[C_6mim]^+$	$[C_{10}mim]^+$	$[C_4mmim]^+$	$[C_4py]^+$	$[C_4m_{(3)}py]^+$	$[C_4mpyrr]^+$	$[P_{66614}]^+$
$[BF_4]^-$		24		25	26	26	27	28			
$[C_1SO_4]^-$	29	30		31						32	
$[NTf_2]^-$	33	24	34	35			36	37	37	38	39
$[PF_6]^-$			40	41	26	26					
$[DCA]^-$									42		39

Table 2. Ionic Liquids, Their Corresponding Purities, and Experimental Details for Data Collection Reported in Each Reference[a]

ionic liquid	MW (g/mol)	Temp. range (K)	no. of data points	equipment	purity (wt %)	water content (ppm)	halide content (ppm)	ref
$[C_1mim][C_1SO_4]$	208.24	293.15−343.15	6	capillary tube	NA	<300	NA	29
$[C_1mim][NTf_2]$	377.28	298.15−343.15	6	cone−plate viscometer	NA	<10	NA	33
$[C_2mim][BF_4]$	197.97	293.15−343.15	7	capillary tube	NA	<30	<30	24
$[C_2mim][C_1SO_4]$	222.26	293.15−343.15	7	concentric cylinders viscometer	99	<100	NA	30
$[C_2mim][NTf_2]$	391.31	293.15−343.15	6	capillary tube	NA	<30	<30	24
$[C_3mim][NTf_2]$	405.34	318.15−343.15	5	capillary tube	>99	50	53	34
$[C_3mim][PF_6]$	270.16	318.15−343.15	5	capillary tube	>99	78.75	<100	40
$[C_4mim][BF_4]$	226.02	293.15−343.15	7	concentric cylinders viscometer	>99	146	NA	25
$[C_4mim][C_1SO_4]$	250.32	293.15−343.15	7	capillary tube	NA	<300	NA	31
$[C_4mim][NTf_2]$	419.36	318.15−343.15	5	concentric cylinders viscometer	99	1156	NA	35
$[C_4mim][PF_6]$	284.18	318.15−343.15	5	capillary tube	>99	<100	NA	41
$[C_6mim][BF_4]$	254.08	313.15−363.15	6	cone−plate viscometer	NA	NA	NA	26
$[C_6mim][PF_6]$	312.24	313.15−363.15	6	cone−plate viscometer	NA	NA	NA	26
$[C_{10}mim][BF_4]$	310.18	313.15−363.15	6	cone−plate viscometer	NA	NA	NA	26
$[C_{10}mim][PF_6]$	368.34	313.15−363.15	6	cone−plate viscometer	NA	NA	NA	26
$[C_4mmim][BF_4]$	240.05	298.15−353.15	7	falling/rolling ball viscometer	>99.8	NA	NA	27
$[C_4mmim][NTf_2]$	433.39	298.15−353.15	7	concentric cylinders viscometer	>98	24	NA	36
$[C_4py][BF_4]$	223.02	298.15−353.15	7	falling/rolling ball viscometer	NA	625	<100	28
$[C_4py][NTf_2]$	416.36	298.15−353.15	7	concentric cylinders viscometer	>99	<100	<100	37
$[C_4m_{(3)}py][NTf_2]$	430.39	298.15−348.15	6	capillary tube	>99	<100	<100	37
$[C_4m_{(3)}py][DCA]$	216.28	298.15−348.15	6	capillary tube	NA	<730	<1000	42
$[C_4mpyrr][C_1SO4]$	253.36	298.15−343.15	6	capillary tube	>99	<600	NA	32
$[C_4mpyrr][NTf_2]$	422.41	298.15−343.15	6	concentric cylinders viscometer	>99.9	3.6	<1	38
$[P_{66614}][NTf_2]$	764.00	298.15−348.15	6	concentric cylinders viscometer	>99	33.6	NA	39
$[P_{66614}][DCA]$	549.90	298.15−348.15	6	concentric cylinders viscometer	>99	151	NA	39

[a]MW, molecular weight; NA, not available.

twenty-six ionic liquids, compromising nine 1-alkyl-3-methylimidazolium cations and eight anions with a temperature range from 258.15 to 433.15 K at atmospheric pressure; 304 data points were correlated with R^2 being 0.9888. Among those, eight data points had deviations higher than 30%. Gardas and Coutinho[17] developed a group contribution method based on the Orrick-Erbar[18] model. The optimum values of group parameters of eight anions were obtained by minimizing an objective function. The cation was split into the heterocyclic ring, methylene, and methyl groups. The relative group contributions of heterocyclic rings, methylene, and methyl groups were then calculated. A mean percent deviation (MPD) of 7.7% was yielded with a maximum deviation just under 28% for a database of ca. 500 data points for 29 ILs. Daniel et al.[19] also used the group contribution method based on the Orrick−Erbar equation[18] for the estimation of a particular group of ILs, such as the magnetic ionic liquids (MILs). Five points for each IL ($[P_{66614}]_3[GdC_{l6}]$, $[P_{66614}]_2[MnCl_4]$, $[P_{66614}][FeCl]_4$ and $[P_{66614}]_2[CoCl_4]$) were used with a result of 7.64% of MPD.

It has been reported that Eyring's theory[20] was coupled with other models for the viscosity correlation of binary mixtures containing ILs.[21−23] Wang et al.[21] calculated the viscosity of ILs with cosolvent mixtures using the Eyring−NRTL and Eyring−UNIQUAC equations. The results for 1014 data points of 35

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binary systems have been compared. Eyring−UNIQUAC gave a better accuracy with the RAAD being 2.61% than the Eyring−NRTL equation (3.5%). He et al.[22] performed three methods (Eyring−Wilson, Eyring−NRTL and Eyring−UNIQUAC) for the correlation of binary mixtures with ILs by collecting 1560 data points of 49 mixtures. The results showed that the Eyring−Wilson equation gave almost the same accuracy as the Eyring−UNIQUAC equation and a better performance than the Eyring−NRTL equation. The Eyring−Wilson equation has a more simple mathematical form than the Eyring−UNIQUAC equation. Atashrouz et al.[23] proposed another model (Eyring−MTSM), which also had a higher accuracy than the Eyring−NRTL model.

All these methods proved their applicability to some particular family of ionic liquids. However, many of the current available methods are not generic and they are not effective at predicting the viscosity over a range of ILs structure, temperature, even at atmospheric pressure.

In this paper, we developed a methodology based on the UNIFAC−VISCO group contribution model to determine the viscosity of ILs as a function of the temperature from 293.15 to 363.15 K at 0.1 MPa. To date, the UNIFAC−VISCO method has not been used to estimate the viscosity of pure or mixed ionic liquids. In our original approach, the anion and cation of each IL are considered as individual groups. A set of experimental data available in the literature[24−39,40,41,42] was used to determine the UNIFAC−VISCO model parameters for each anion and cation. Successively, ILs were constructed by different combinations of cations and anions and their viscosities were determined. This method was then extended for the determination of the viscosity of binary mixtures of ILs as the function of the composition and temperature at 0.1 MPa. Similarly, the anions and cations within the mixture were treated as individual groups.

The new method proposed herein is applicable to any family of ILs; any cation/anion structure and combination. Therefore, it is a generic method. The VFT parameters obtained for one cation (or anion) from one IL can be used for the prediction of viscosity of any other ILs or ILs mixture containing the same cation (or anion). The group interaction potential energy parameters calculated by fitting the viscosity of one IL can be used in any other mixture of ILs which happens to have same anion−cation combination. But experimental data is needed to determine any remaining unknown group interaction potential energy parameters within the IL mixture.

In this paper, we report the successful development of this method for the prediction of viscosity of pure ILs and their mixtures as the function of the IL structure, composition, and temperature at 0.1 MPa.

2. DATA COLLECTION

To develop the UNIFAC−VISCO-based model for ILs, 25 different ILs from 19 different references (154 data points) were chosen.[24−42] The selected ILs are among the most commonly studied with a large number of experimentally available viscosity data in the literature. This work is a proof of concept study to demonstrate the potential of the proposed method for the prediction of the viscosity of ILs. Therefore, a limited number of ILs were used by carefully selecting the data from the available literature depending on the purity, viscosity measurement method, and temperature.

The cations used are imidazolium, pyridinium, pyrrolidinium, and phosphonium-based structures. Five different inorganic anions are used, for example, bis(trifluoromethylsulfonyl)imide ($[NTf_2]^-$), hexafluorophosphate ($[PF_6]^-$), and dicyanamide ($[DCA]^-$). Selected cations and anions are listed in Table 1 along with the references from which the experimental viscosity data were taken. The temperature range, number of data points in each reference, molecular weight, purity of ionic liquids, contents of impurity, and measurement methods are summarized in Table 2.

The accuracy of the viscosity measurements strongly depends on the purity of the ionic liquid used. The most common impurities found within ILs include water, halides (chloride, bromide, iodide), metals (lithium, sodium, etc.), and unreacted reagents.[43] Specifically chloride and water have a dramatic effect on the viscosity of ILs. Typically the presence of chloride increases generally the viscosity of the IL. Conversely water decreases (generally) the ILs viscosity.[44] In a comparison of the IL $[C_4mim][BF_4]$ reported by Nikitina et al.[45] and by Vakili et al.[25] up to a 15% difference in its viscosity is observed especially at lower temperatures (see Figure S1 of the Electronic Supporting Information, ESI). Therein, the water content of $[C_4mim][BF_4]$ was reported to be below 15 ppm in the former study and an order of magnitude higher (146 ppm) in the latter study. Therefore, the viscosity values taken from Vakili et al.[25] are smaller than those from Nikitina et al.[45] at any same temperature, due to the increased concentration of water. Similarly, the effects of different batches of a common IL on the viscosity can be seen by comparing the viscosity data of $[C_4py][BF_4]$ samples (Figure S2 of ESI). Larriba et al.[46] purchased $[C_4py][BF_4]$ samples from Iolitec GmbH with a water level lower than 100 ppm and chloride content less than 100 ppm. While Mokhtarani et al.[28] synthesized $[C_4py][BF_4]$ in their own laboratory with water content of 625 ppm and bromide content less than 100 ppm. The viscosities of these two samples were both determined with an Anton Paar automated microviscometer (AMVn).

The viscosity measurement techniques are another source of deviation in the accuracy of viscosity data in literature. García-Mardones et al.[47] also obtained $[C_4py][BF_4]$ from Iolitec; however, García-Mardones et al.[47] used a set of Ubbelohde viscosimeters to measure the viscosity of $[C_4py][BF_4]$. At 293.15 K, the value measured by Larriba et al.[42] (227.1 mPa·s) is 1.7% higher than the viscosity measured by Mokhtarani et al.[28] and 2.8% higher than the viscosity measured by García-Mardones et al.[47] This clearly shows that in some cases the experimental techniques have an even more dramatic effect on the measured viscosities than the water content when the IL is dried under vacuum prior to its use.

Discrepancies in the experimental data affect the quality of the correlation and thus the development of the predictive method. Therefore, in this study, we have only selected experimental data with the lowest halide and water impurity. As a proof of concept study, we selected data with low levels of impurities in order to reduce errors. The quantity of water, halide, and impurity levels are given in Table 2. In addition, to eliminate the negative effect of systematic errors for the development of our new method, we used only one data set from a single reference for each IL to develop the proposed UNIFAC−VISCO-based model.

3. DEVELOPMENT OF THE UNIFAC−VISCO METHOD FOR IONIC LIQUIDS

3.1. Calculation of the Viscosity by the UNIFAC−VISCO Method. The UNIFAC−VISCO model is a group

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contribution model developed by Chevalier et al.[48,49] to predict the viscosities of liquid mixtures. This model is based on the theory of Eyring and the UNIFAC group contribution model proposed originally by Fredenslund et al.[50]

The viscosity calculation (eq 1) by using UNIFAC−VISCO method is described as follows:[48,49,51]

$$\ln(\mu) = \sum_{i=1}^{C} x_i \ln\left(\mu_i \frac{V_i}{V_m}\right) + \frac{g_c^E}{\mathcal{R}T} - \frac{g_r^E}{\mathcal{R}T} \quad (1)$$

where μ is the mixtures viscosity (mPa·s); subscript i represents the component; C is the total number of components; x_i is the mole fraction of the component i. V_i is the molar volume (m^3/kmol) of the pure component i, while V_m is molar volume (m^3/kmol) of the mixture. $\mathcal{R}$ is the gas constant (J/mol·K) and T is temperature (K). g_c^E and g_r^E are the combinatorial and the residual contribution terms of the UNIFAC−VISCO method, respectively.

The combinatorial contribution term (eq 2) is defined as

$$\frac{g_c^E}{\mathcal{R}T} = \sum_i x_i \ln \frac{\phi_i}{x_i} + \frac{z}{2} \sum_i x_i q_i \ln \frac{\theta_i}{\phi_i} \quad (2)$$

where z is a coordinate value equal to 10 and x_i is the mole fraction of the component i. ϕ_i is the molecular volume fraction of component i; q_i represents the van der Waals' surface area of component i; and θ_i is the molecular surface area fraction of component i.

θ_i and ϕ_i can be obtained by the following eqs 3 and 4:

$$\theta_i = \frac{x_i q_i}{\sum_j x_j q_j} \quad (3)$$

$$\phi_i = \frac{x_i r_i}{\sum_j x_j r_j} \quad (4)$$

where subscript i and j represent the components, q_i and q_j represent the van der Waals' surface area of components i and j, respectively, and r_i and r_j represent the van der Waals' volume of components i and j, respectively.

The surface area (q) and the volume (r) can be determined by the following eqs 5 and 6:

$$q_i = \sum_{k=1}^{N} n_{i,k} Q_k \quad (5)$$

$$r_i = \sum_{k=1}^{N} n_{i,k} R_k \quad (6)$$

where subscript k denotes the groups; $n_{i,k}$ is the total number of kth group present in component i; N is the total number of groups present; Q_k is the group surface area parameter; and R_k is the group volume parameter.

The residual contribution (eq 7) term is defined as

$$\frac{g_r^E}{\mathcal{R}T} = \sum_{i=1}^{C} x_i \left[\sum_{m=1}^{N} n_{m,i} (\ln \gamma_m - \ln \gamma_{m,i})\right] \quad (7)$$

where C is the total number of components; x_i is the fraction of component i in the mixture; N is the total number of groups; n_m and γ_m refer to the group values in the mixture, and $n_{m,i}$ and $\gamma_{m,i}$ refer to the group values in pure-component.

$\ln \gamma_m$ represents the residual activity coefficient and can be obtained by using eq 8:

$$\ln \gamma_m = Q_m \left[1 - \ln\left(\sum_{i=1}^{N} \Theta_i \Psi_{i,m}\right) - \sum_{i=1}^{N} \frac{\Theta_i \Psi_{m,i}}{\sum_{j=1}^{N} \Theta_j \Psi_{j,i}}\right] \quad (8)$$

where N is the total number of groups present; Θ_i represents the surface area fraction for group i; and $\Psi_{m,i}$ represents the group interaction parameters.

The Θ values for each group both in mixture and in pure component can be calculated using eq 9:

$$\Theta_m = \frac{x_m Q_m}{\sum_{i=1}^{N} X_i Q_i}, \quad m = 1, 2, 3...N \quad (9)$$

where the subscripts represent the groups.

The group interaction parameters (Ψ) are then calculated by using eq 10:

$$\Psi_{mn} = \exp\left(-\frac{\alpha_{mn}}{298.15}\right) \quad (10)$$

where α_{mn} are group interaction potential energy parameters between the groups m and n. It is important to note that the values for the group interaction parameters α_{mn} and α_{nm} are not the same.

3.2. Calculation of Ionic Liquid Viscosity by the UNIFAC−VISCO Method. The viscosity of the pure ILs is calculated by the UNIFAC−VISCO method by following an original approach, in which the cation and anion, constituting each ionic liquid, are regarded as individual groups. In this case, each component is made up of a single group (either cation or anion). Sample calculations for a pure IL and a binary mixture of ILs by using our model based on the UNIFAC−VISCO method are given in the Supporting Information.

The first set of parameters required for the calculation of IL viscosity using the UNIFAC−VISCO method is the molar volume (V_i) of pure components and the molar volume of their mixture (V_m). For a single ionic liquid, these correspond to the effective molar volume of the cation and anion (i.e., components) and the molar volume of pure ionic liquid, respectively. It is not straightforward to obtain the effective molar volumes of ions. However, in our previous study,[43,52] we developed a group contribution model to predict the volumetric properties of ILs.

In this case, the mixture of anion and cation is considered to be ideal.[43,52] The quadratic eq eq 11 was used to fit the experimental volumetric data as a function of temperature at a reference pressure (0.1 MPa).

$$V_m(T, p_{ref}) = \sum_{i=0}^{2} (b_i \cdot (T)^i_{p_{ref}}) \quad (11)$$

where p_{ref} = 0.1 MPa and b_i is the fitting parameters.

The Jacquemin et al.[43,52] method has been then extended to calculate the effective molar volumes of individual cations and anions. Fitting parameters for the calculation of the effective molar volumes of selected ions at 0.1 MPa used in this study are given in Table S1 of the Supporting Information. The effective molar volumes of the cations (V_c^*) and anions (V_a^*) can be calculated as a function of temperature and pressure by following eq 11 and eq 12.

$$V_m(T^*, p_{ref}) = V_c^*(T^*, p_{ref}) + V_a^*(T^*, p_{ref}) \quad (12)$$

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$$V^*_{\text{ion}}(T^*, p_{\text{ref}}) = \sum_{i=0}^{2} (a_i \cdot (T^*)^i_{p_{\text{ref}}}) \quad (13)$$

where $T^* = T - 298.15$, $p_{\text{ref}} = 0.1$ MPa, and a_i is the effective molar volume group contribution parameter as described by Jacquemin et al.[43,52]

The second set of parameters required for the calculation of IL viscosity using the UNIFAC−VISCO method is the cations and anions volume R and surface area Q parameters. The R and Q values of cations and anions used in this study were obtained by using the COSMO*therm* software (version C30_1501) by following the methodology previously described by our group[53] and are given in Table S2 of the Supporting Information.

In the UNIFAC−VISCO method, individual component viscosities, that is, the effective viscosity of each ion, are required (see eq 1). Furthermore, in this work, the temperature dependence on the effective viscosity of each ion, μ_{ion}, is represented by the Vogel−Fulcher−Tamman (VFT) type fitting equation:

$$\mu_{\text{ion}} = A \cdot \exp\left[\frac{B}{T - T_0}\right] \quad (14)$$

where A, B, and T_0 are the fitting parameters of the effective viscosity of each ion.

Another set of parameters required in the UNIFAC−VISCO method are the mole fractions of components. In our approach we assumed that the components, i.e. the cations and anions, contribute equally to the viscosity of the pure ionic liquid or the mixture of ionic liquids. Therefore, in the calculation of the viscosity of pure ionic liquids, the mole fractions of ions were taken as equal to 0.5. Similarly, in the calculation of binary mixtures of ionic liquids, the mole fraction of each ion is taken as equal to 0.25.

The viscosity data were then correlated by minimizing the objective function (eq 15) using the Marquardt[54] optimization technique to estimate the unknown parameters of the UNIFAC−VISCO group interaction potential energy parameters and ions VFT fitting parameters:

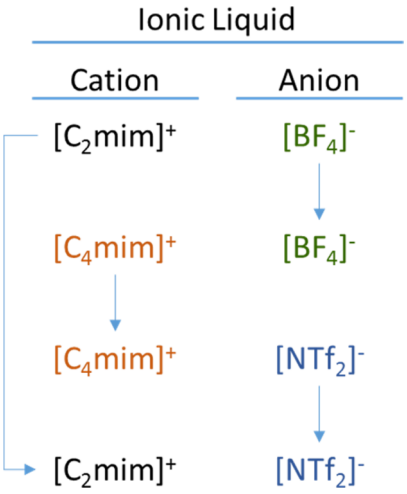
$$\text{OF} = \frac{1}{M} \sum_{i=1}^{M} \left(\frac{\mu_{\text{exp}} - \mu_{\text{calc}}}{\mu_{\text{exp}}} \right)^2 \rightarrow \min \quad (15)$$

where M is the number of data points; μ_{exp} and μ_{calc} are the experimental and calculated viscosity data, respectively.

For each ionic liquid, eight parameters are required for the calculation of viscosity by the UNIFAC−VISCO method. These parameters are the group interaction potential energy parameters of cation and anion (α_{mn}, α_{nm}) and the VFT fitting parameters for each cation and anion defining the temperature dependency of viscosity (A, B, T_0 for each cation and anion). During this work, the Solver tool in Microsoft Excel was used to obtain initial estimates for required parameters. These parameters were then used as initial guess values in a MATLAB script, which was developed to achieve the calculation process by using a nonlinear least-squares regression method.

The accuracy of the fitting parameters depends on the available number of experimental data points. On the basis of our approach, the VFT parameters and group interaction potential energy parameters are cation and anion specific and thus must be the same irrespective of the IL structure. Therefore, performing the regression analysis of ionic liquids with common cations and anions decreases the number of unknown parameters relative to the available experimental data. Herein, first we used four ILs with common ions for calculations accordingly. An example of this approach is shown in Scheme 1.

Scheme 1. Example of the Methodology Used during the Regression Analysis



For example, the following four ionic liquids; $[C_2mim][BF_4]$, $[C_4mim][BF_4]$, $[C_2mim][NTf_2]$, and $[C_4mim][NTf_2]$ are based on two different cations ($[C_2mim]^+$ and $[C_4mim]^+$) and two different anions ($[BF_4]^-$ and $[NTf_2]^-$). A total of 20 unknown parameters, that is, two group interaction potential energy parameters for each IL and three sets of VFT parameters for each individual ion, were calculated by regression analysis. This is a significant reduction in the number of parameters required and consequently the number of initial guess values in order to correlate UNIFAC−VISCO based model. Since VFT parameters do not depend on temperature, more experimental data at different temperatures improve the quality of the fit, because the number of fitting parameters relative to the available experimental data decreases significantly.

Sample viscosity calculations for pure ILs and binary mixture of ILs and MATLAB files are provided in the Supporting Information. First MATLAB program (Filename: IonicLiquidViscosityCalculator) contains all parameters (binary interaction and VFT parameters) estimated during this study. This program can be used to determine the viscosity of selected ionic liquids and it could be further extended to include additional ILs. Another set of MATLAB program files (PureILs and BinaryILs) were developed for the estimation of UNIFAC−VISCO parameters by the built-in functions of least-square method.

4. RESULTS AND DISCUSSION

Group interaction potential energy and VFT parameters were estimated by following the regression analysis (eq 15) of the experimental data for selected pure ILs (see Tables 1 and 2). The calculated binary group interaction potential energy parameters (α_{mn}, α_{nm}) for the cation and anion pairs are given in Table 3, while the VFT parameters of selected cations and anions are given in Table 4.

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Table 3. Calculated Binary Interaction Parameters of the Selected Cations and Anions

m/n	$[C_1mim]^+$	$[C_2mim]^+$	$[C_3mim]^+$	$[C_4mim]^+$	$[C_6mim]^+$	$[C_{10}mim]^+$	$[C_4mmim]^+$	$[C_4py]^+$	$[C_4m_{(3)}py]^+$	$[C_4mpyrr]^+$	$[P_{66614}]^+$	$[BF_4]^-$	$[C_1SO_4]^-$	$[NTf_2]^-$	$[PF_6]^-$	$[DCA]^-$
$[C_1mim]^+$	0												−110.98	−501.14		
$[C_2mim]^+$		0			−268.48							640.24	199.49	−440.63		
$[C_3mim]^+$			0											1079.2	5109	
$[C_4mim]^+$				0	−2.044							6621.9	412.52	468.31	1493.5	
$[C_6mim]^+$		526.09		92.09	0							608.51			481.62	
$[C_{10}mim]^+$						0						930.63			888.41	
$[C_4mmim]^+$							0					2542.9		21.28		
$[C_4py]^+$								0				853.75		135.61		
$[C_4m_{(3)}py]^+$									0					697.53		1205.8
$[C_4mpyrr]^+$										0			459.77	−127.39		
$[P_{66614}]^+$											0			1604.1		17932
$[BF_4]^-$		−344.33		−525.06	−589.81	−690.34	−620.52	−672.1				0	−132.74		35.31	
$[C_1SO_4]^-$	−63.94	−268.73		−457.11					−530.52			65.44	0			
$[NTf_2]^-$	1240.8	952.54	−485.25	−379.05			−86.07	−375.63	−331.41	−64.14	−462.47			0		
$[PF_6]^-$			−628.86	−591.16	−564.61	−657.16						26.40			0	
$[DCA]^-$									−352.31		−627.51					0

Table 4. VFT Fitting Parameters of the Selected Cations and Anions

cation/anion	A (mPa·s)	B (K)	T_0 (K)
$[C_2mim]^+$	0.1242	963.7	122.1
$[C_4mim]^+$	0.0617	981.2	155.5
$[C_3mim]^+$	0.2703	501.9	191.9
$[C_4m_{(3)}py]^+$	0.2641	791.9	186.7
$[P_{66614}]^+$	5.2975	658.2	172.4
$[C_4mmim]^+$	0.1219	865.0	199.0
$[C_4py]^+$	0.0353	710.7	187.6
$[C_6mim]^+$	0.0065	1639	124.2
$[C_{10}mim]^+$	0.0091	1671	121
$[C_1mim]^+$	0.6941	330.0	204.5
$[C_4mpyrr]^+$	0.0469	932.7	178.9
$[BF_4]^-$	3.7391	352.1	202.4
$[C_1SO_4]^-$	0.8313	675.3	186.5
$[NTf_2]^-$	1.2222	548.7	125.3
$[PF_6]^-$	3.2320	370.2	219.4
$[DCA]^-$	2.6871	370.5	118.1

The quality of the regression was then determined by calculating the relative absolute average deviations (RAAD, eq 16) between the calculated and the experimental viscosity data.

$$\mathrm{RAAD} = 100 \times \frac{1}{M} \sum_{i}^{M} \left| \frac{\mu_{\mathrm{exp}} - \mu_{\mathrm{cal}}}{\mu_{\mathrm{exp}}} \right| \tag{16}$$

The RAAD values for the regression of pure ILs and binary mixtures of ILs are reported in Tables 5 and 6, respectively. For the regression of the pure ILs, it appears that the RAADs are lower than 1% for all the investigated ILs except in the case of the $[C_{10}mim][BF_4]$ (RAAD = 1.61%) and $[C_4py][BF_4]$ (RAAD = 1.25%). This shows that the regression of the viscosity data of pure ILs using the UNIFAC−VISCO method is achieved with accuracy better than 1.7% with the respect of the selected experimental data. For the calculation of the relative average absolute deviation, 1.7%, all the experimental data were used. This is the accuracy obtained by using the carefully selected data to develop the model. Therefore, the reported accuracy of 1.7% represents the correlation ability of the model.

The comparison of experimental and calculated viscosity data with our model is shown in Figure 1 in the case of the pure ILs investigated during this work (see Tables 1 and 2). A good agreement between the UNIFAC−VISCO model and the experimental data is observed (see Figure 1 and Figure S3 of the Supporting Information).

A limited number of viscosity data for binary mixtures of ionic liquids has been reported in the literature to date. By using the group interaction potential energy and VFT parameters obtained by the regression of the pure ILs and by following the same methodology, the viscosity of binary mixtures of ILs were then correlated by the UNIFAC−VISCO model. The viscosity data of four binary mixtures of ILs reported in the literature,[55] were used to exemplify the feasibility to extend our approach in the case of the mixture of two pure ILs. The compositions of the mixtures, temperature range, and number of data reported by Navia et al.[55] are summarized in Table 6. Herein one set of data for each binary mixture was correlated for the group interaction potential energy parameters (see Table 7). The other data of each mixture were used to compare with the predicted viscosities.

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Table 5. Relative Absolute Average Deviation (RAAD) of the Calculated Viscosity from the Experimental Viscosity Data for Selected ILs

ionic liquid	RAAD (%)	ionic liquid	RAAD (%)	ionic liquid	RAAD (%)	ionic liquid	RAAD (%)	ionic liquid	RAAD (%)
$[C_1mim][C_1SO_4]$	0.49	$[C_3mim][NTf_2]$	0.19	$[C_4mim][PF_6]$	1.02	$[C_4mmim][BF_4]$	0.33	$[C_4m_{(3)}py][DCA]$	0.75
$[C_1mim][NTf_2]$	0.60	$[C_3mim][PF_6]$	0.16	$[C_6mim][BF_4]$	0.54	$[C_4mmim][NTf_2]$	0.77	$[C_4mpyrr][C_1SO4]$	0.43
$[C_2mim][BF_4]$	0.20	$[C_4mim][BF_4]$	0.37	$[C_6mim][PF_6]$	0.60	$[C_4py][BF_4]$	1.25	$[C_4mpyrr][NTf_2]$	0.73
$[C_2mim][C_1SO_4]$	0.08	$[C_4mim][C_1SO_4]$	0.11	$[C_{10}mim][BF_4]$	1.61	$[C_4py][NTf_2]$	0.31	$[P_{66614}][NTf_2]$	0.26
$[C_2mim][NTf_2]$	0.58	$[C_4mim][NTf_2]$	0.27	$[C_{10}mim][PF_6]$	0.48	$[C_4m_{(3)}py][NTf_2]$	0.09	$[P_{66614}][DCA]$	0.14

Table 6. Binary Viscosity Data Adapted from Navia et al.[55]

binary system	mole fraction range (x)	temp range (K)	no. of data points
$x[C_6mim][BF_4] + (1 - x)[C_2mim][BF_4]$	0.0978−0.9455	298.15−308.15	117
$x[C_4mim][BF_4] + (1 - x)[C_4mim][C_1SO_4]$	0.1209−0.9447	298.15−308.15	117
$x[C_4mim][PF_6] + (1 - x)[C_4mim][BF_4]$	0.0568−0.945	298.15−308.15	117
$x[C_6mim][BF_4] + (1 - x)[C_4mim][BF_4]$	0.1083−0.946	298.15−308.15	99

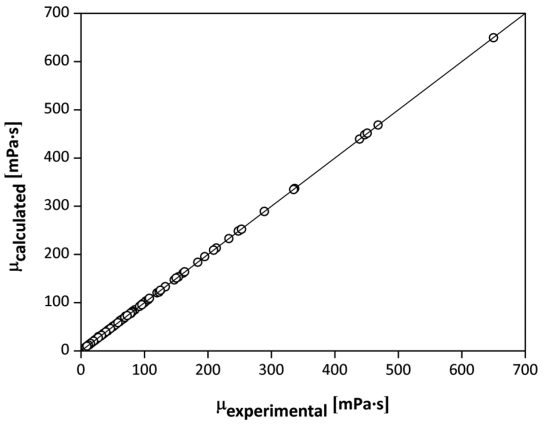

Figure 1. Comparison of experimental viscosity and predicted viscosity for pure ionic liquids.

The prediction result is highlighted by the RAAD values, reported in Table 8, which is 5% for all reported binary data published by Navia et al.[55]

In addition the parity plot given in Figure 2 shows good agreement between the experimental data and calculated viscosity values by using the UNIFAC−VISCO model with the exception of a visual larger deviation at higher mole fraction of $[C_4mim][PF_6]$ in the binary system ($[C_4mim][PF_6]$ and $[C_4mim][BF_4]$). This good agreement is also attested by the calculated relative deviations between the experimental and predicted viscosity data for selected binary ILs as shown in Figure S4 of the Supporting Information.

5. CONCLUSIONS

An original method for the determination of the viscosity of ionic liquids and mixtures of ionic liquids was developed. The model is based on the UNIFAC−VISCO model in which the cations and anions constituting the ionic liquids are regarded as individual components. The regression analysis was performed with single ionic liquids to estimate the group interaction potential energy and VFT parameters of each ion. The RAAD is below 1.7% for all ionic liquids studied. The viscosity of binary mixtures of ionic liquids was then calculated and

Table 8. Relative Absolute Average Deviations (RAAD) of Viscosity Predictions from the Experimental Viscosity Data for Binary Mixtures of ILs

binary system	RAAD (%)
$x[C_6mim][BF_4] + (1 - x)[C_2mim][BF_4]$	3.2
$x[C_4mim][BF_4] + (1 - x)[C_4mim][C_1SO_4]$	3.8
$x[C_4mim][PF_6] + (1 - x)[C_4mim][BF_4]$	5.4
$x[C_6mim][BF_4] + (1 - x)[C_4mim][BF_4]$	8.2
all mixtures	5.0

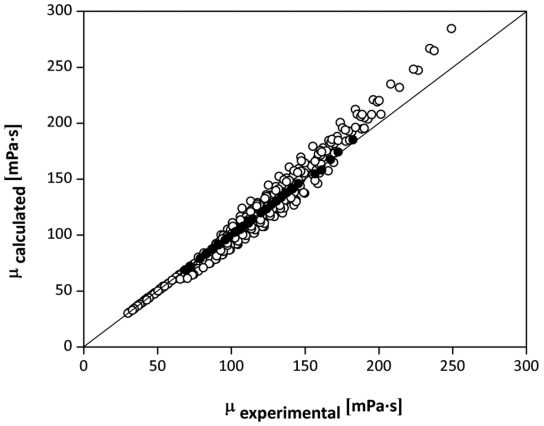

Figure 2. Comparison of experimental viscosity and predicted viscosity for binary ionic liquids where data used for developing correlation (●) and predicted data (○) are shown.

Table 7. Selected sets of binary mixtures of ILs. Experimental data were taken from Navia *et al*[55] for regression

binary system	mole fraction (x)	temp range (K)	no. of data points
$x[C_6mim][BF_4] + (1 - x)[C_2mim][BF_4]$	0.5939	298.15 to 308.15	9
$x[C_4mim][BF_4] + (1 - x)[C_4mim][C_1SO_4]$	0.648	298.15 to 308.15	9
$x[C_4mim][PF_6] + (1 - x)[C_4mim][BF_4]$	0.5974	298.15 to 308.15	9
$x[C_6mim][BF_4] + (1 - x)[C_4mim][BF_4]$	0.7005	298.15 to 308.15	9

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compared with experimental data available in the literature. It turned out that the RAAD is 5% for all mixtures. This shows that the UNIFAC−VISCO model can be used to correlate and predict the viscosities of pure ionic liquids as well as mixtures of ionic liquids with great accuracy.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jced.6b00161.

Comparisons of two experimental data sets available in the literature in the case of the $[C_4mim][BF_4]$ and $[C_4py][BF_4]$ are reported in Figures S1−S2, respectively. The relative deviations between the experimental and predicted viscosity data for pure ionic liquids and selected binary mixtures of ILs are reported in Figures S3−S4, respectively. Furthermore, all effective molar volume parameters, R and Q values for each ion estimated during this work, are tabulated in Tables S1−S2. Examples of the viscosity calculations for a pure IL and a binary mixture of ILs are given. Component viscosities, component molar volumes, groups, area fractions, volume fractions, group interactions, group fractions required for the viscosity calculation are given in Tables S3−13 (PDF)

Matlab files (ZIP)

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Notes

The authors declare no competing financial interest.

■ ABBREVIATIONS

Cations

$[C_1mim]^+$ 1,3-dimethylimidazolium
$[C_2mim]^+$ 1-ethyl-3-methylimidazolium
$[C_3mim]^+$ 1-propyl-3-methylimidazolium
$[C_4mim]^+$ 1-butyl-3-methylimidazolium
$[C_6mim]^+$ 1-hexyl-3-methylimidazolium
$[C_{10}mim]^+$ 1-decyl-3-methylimidazolium
$[C_4mmim]^+$ 1-butyl-2,3-methylimidazolium
$[C_4py]^+$ 1-butylpyridinium
$[C_4m_{(3)}py]^+$ 1-butyl-3-methylpyridinium
$[C_4mpyrr]^+$ 1-butyl-1-methylpyrrolidinium
$[P_{66614}]^+$ trihexyl(tetradecyl)phosphonium

Anions

$[BF_4]^-$ tetrafluoroborate
$[NTf_2]^-$ bis(trifluoromethylsulfonyl)amide
$[GdCl_6]^{3-}$ hexachlorogadolinium
$[MnCl_4]^{2-}$ tetrachloromanganese
$[FeCl_4]^-$ tetrachloroferrate
$[CoCl_4]^{2-}$ tetrachlorocobalt
$[C_1SO_4]^-$ methylsulfate
$[PF_6]^-$ hexafluorophosphate
[DCA] dicyanamide

Nomenclature

Roman Letters

a_i Tait equation parameter
b_i Tait equation parameter
A VFT equation parameter
B VFT equation parameter
C total number of components in UNIFAC−VISCO method
g_c^E combinatorial contribution term in UNIFAC−VISCO method
g_r^E residual contribution term in UNIFAC−VISCO method
$n_{i,k}$ total number of k^{th} group present in component i
N total number of groups
p_{ref} reference pressure (0.1 MPa)
q_i van der Waals' surface area of component i
Q_k group surface area parameter
r_i van der Waals' volume of component i
R_k group volume parameter
$\mathcal{R}$ gas constant (J/mol·K)
T temperature (K)
T_0 VFT equation parameter
V_i pure-component molar volume (m^3/kmol)
V_m mixture molar volume (m^3/kmol)
x_i mole fraction of the component i
z coordinate value in UNIFAC−VISCO method

Greek Letters

α_{mn} group interaction potential energy parameter between groups m and n
γ_m residual activity coefficient
θ_i molecular surface area fraction of component i
Θ_i surface area fraction for group i
μ viscosity of mixture (mPa·s)
μ_i viscosity of component i
μ_{exp} viscosity experimentally measured
μ_{cal} viscosity calculated by our method
ρ_{IL} density
ϕ_i molecular volume fraction of component i
$\Psi_{m,i}$ group interaction parameter

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